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(54) **PROCEDES DE SEPARATION DU CUIVRE ET DES METAUX LOURDS CONTENUS DANS DES RESIDUS ET DES SCORIES D'ORDURES INCINEREES**

(54) **PROCESS FOR THE SEPARATION OF COPPER AND HEAVY METALS FROM INCINERATED GARBAGE RESIDUE AND SLAG**

(57) Selon un procédé permettant de séparer du cuivre et des métaux lourds contenus dans des résidus et des scories d'ordures incinérées, les résidus et les scories résultant de l'incinération ou de la pyrolyse d'ordures sont chauffés à plus de 650°C, dans des conditions de réaction, avec des substances contenant du chlore ou des chlorures, telles que des résidus de purification de gaz de fumée, du $CaCl_2$ résultant de la production de soude, du sel de cuisine, des solvants organiques ou des boues contenant du chlore, puis les chlorures de CU et les chlorures de métaux lourds volatiles, tels que $PbCl_2$ ou $ZnCl_2$, sont extraits en phase gazeuse.

(57) In a process for the separation of copper and heavy metals from incinerated garbage residue and slag, the residue and slag from garbage incineration or pyrolysis is heated to over 650°C under reducing conditions together with substances containing chlorine or chlorides, such as flue gas cleaning residues, $CaCl_2$ from the soda production, cooking salt, organic solvents or electroplating sludge containing chlorine, whereupon Cu-chlorides and volatile heavy metal chlorides, such as $PbCl_2$ or $ZnCl_2$, are drawn off in the gas phase.

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Abstract:

In a method for separating copper and heavy metals from waste incineration residues and slags, the waste incineration and/or pyrolysis residues and slags, together with chlorine and/or chloride-containing substances, such as smoke gas purification residues, $CaCl_2$ from soda production, common salt, chlorine-containing organic solvents or sludges derived from electroplating, are heated to above 650°C under reducing conditions, whereupon Cu chlorides and volatile heavy metal chlorides, such as, e.g., $PbCl_2$ or $ZnCl_2$, are drawn off in the gaseous phase.

Method for Separating Copper and Heavy Metals from Waste Incineration Residues and Slags

The invention relates to a method for separating copper and heavy metals from waste incineration residues and slags.

In conventional waste incineration plants as well as waste pyrolysis plants, residues in the form of pyrolysis residues or waste incineration residues or slags incur. As a rule, such slags are relatively acidic and, depending on the provenance of the waste and, in particular, when using industrial waste, such slags mostly are strongly contaminated with heavy metals. The direct utilization of such slags without more or less intensive purification is feasible only at high apparative expenditures.

The invention aims at rendering such heavy-metal-containing waste incineration residues suitable for subsequent processing by which, for instance, in respect of steel slags environmentally compatible hydraulic binders or other valuable substances may be recovered. A slag not directly suitable for metallurgical processes or residues of the above type, in particular, are to be processable to synthetic blast furnace slag having hydraulic properties as well as high-quality carbon-saturated iron alloys. To solve this object, the method according to the invention essentially consists in that the waste incineration and/or pyrolysis residues and slags, together with chlorine and/or chloride-containing substances, such as smoke gas purification residues, $CaCl_2$ from soda production, common salt, chlorine-containing organic solvents or sludges derived from electroplating, are heated to above 650°C under reducing conditions, whereupon Cu chlorides and volatile heavy metal chlorides, such as, e.g., $PbCl_2$ or $ZnCl_2$, are drawn off in the gaseous phase. The fact that the waste incineration residues and slags and/or pyrolysis residues are calcined along with chlorine and/or chloride-containing substances while maintaining reducing conditions during such

roasting allows for the separation of heavy metals in the form of volatile chlorides and the discharging of the same via the gaseous phase. The gaseous phase may be purified in a conventional manner, wherein copper, chloride, bleaching chloride and zinc chloride may be quantitatively retained by filters. At the same time, a method of this type allows for also the working up of other products that are difficult to dispose of, such as chlorine-containing organic solvents as well as smoke gas purification residues or calcium chloride from soda production, wherein, on the whole, a great number of problem substances can be disposed of simultaneously. In principle, the heavy metal chlorides mentioned have relatively low vapour pressures at low temperatures. The vapour pressures of relevant heavy metal chlorides at 600°C are as follows:

Component	Vapour pressure (bar)
$CuCl_2$, $(CuCl)_2$	0.005
$PbCl_2$	0.07
$ZnCl_2$	0.1

In order to ensure safe volatilization at relatively low temperatures, the respective partial pressure must be appropriately lowered, for instance by using a flush gas, or operation must be effected under an at least partial vacuum. Advantageously, the method according to the invention is realized in a manner that flush gases, in particular hot combustion offgases, are used at temperatures of between 650° and 1400° C for discharging the volatile chlorides, thus causing a sufficient volatilization of the heavy metal chlorides to be observed. Alternatively, or in addition to using such a flush gas, operation may also take place in a partially evacuated shaft furnace or a flush gas may be employed at a negative pressure. At a pressure of 1 bar and without using a flush gas, chlorination would have to be effected at temperatures of approximately 1400°C, i.e., at melting temperature.

By the measure taken according to the invention a sufficiently high depletion of heavy metals is ensured in conventional shaft furnaces by means of combustion offgases used as a flush gas, already at temperatures of 850°C, it being advantageously proceeded in a manner that heating of the waste incineration residues and slags to temperatures of approximately 850°C is effected in a shaft furnace or in a rotary tubular kiln.

The recovery of heavy metals from the gaseous phase may be effected in a particularly simple manner by conducting the gaseous phase containing the volatile heavy metal chlorides through a filter and dissolving in water, and/or cementing with iron scrap, the heavy-metal-chloride-containing filter dust, whereupon the heavy-metal chlorides are extracted and/or the heavy metals are separated by fractional electrolysis and/or are fractionally distilled. During the cementation with iron scrap the heavy metal oxides are reduced and iron chloride is formed. During the fractional electrolysis copper, tin, nickel and other metals may be separated individually and in high purities.

In order to ensure the partial pressures required while, at the same time, maintaining reducing conditions, it is advantageously proceeded in a manner that heating is effected in a shaft furnace by means of combustion offgases in countercurrent.

Particularly reasonable further processing from an economic point of view, of the appropriately depleted waste incineration or pyrolysis residues and slags is feasible if, as in accordance with a preferred further development, the heated solid residues are mixed with liquid steel slag or lime marl in amounts of from 10 to 40 % by weight, preferably about 20 % by weight, so as to form a mixed slag, wherein evaporating heavy metals that have remained, such as Pb and Zn, are separated from the gaseous phase and chlorides possibly dissolved in the mixed slag, such as, e.g., $CaCl_2$, are

oxidized under Cl_2 stripping and the mixed slag is reduced above a turbulent Fe bath having a C content ranging between 3 and 4 % by weight. Since the heated residues enter into an acid reaction, it is feasible by mixing with steel slag to at least partially neutralize the extremely basic steel slag, the viscosity being lowered simultaneously. The mixing and neutralization heat allows for the safe evaporation of heavy metals possibly still left. At the same time, an iron bath is sedimented out of the steel slag, it being advantageously proceeded in a manner that the turbulent Fe bath is subjected to a fractional reduction for separating a ferro-chromium alloy. In doing so, the turbulent iron bath must be maintained at the required carbon content of between 3 and 4 % by weight in order to ensure that the desired reduction does actually take place, wherein a total of 1 ton synthetic blast furnace slag and 0.9 ton pig iron may, for instance, be obtained from approximately 0.4 ton calcined slag and 1.6 tons of steel slag. In order to ensure the formation of a suitable cement aggregate, chlorides must be stripped first.

The method for reducingly calcining waste incineration residues and slags in a particularly advantageous manner thus may be combined with an appropriate method for producing synthetic blast furnace slag, since the CO formed on account of the carbon contents required in the iron bath may be utilized particularly well from an energetic point of view. To this end, it is advantageously proceeded in a manner that the CO formed in the reduction of the slag mixture by the carbon dissolved in the Fe bath is used for further burning and heating the mixed slag and/or the residues.

In order to further enhance the quality of the synthetic blast furnace slag and to be able to produce particularly suitable cement aggregates or cement directly, it is advantageously proceeded in a manner that bauxite, or Al_2O_3, is added to the liquid mixed slag.

As already mentioned in the beginning, the partial pressures required for the volatile chlorides may be adjusted either by suitable amounts of flush gas or by applying a subatmospheric pressure.

In the following the invention will be explained in more detail by way of an exemplary embodiment.

A waste slag having the following composition

Component	Portion (%)
SiO_2	43
CaO	13
Al_2O_3	8.5
Fe_2O_3	10
MgO	1.5
Na_2O	3.5
SO_3	1
TiO_2	1.5
Cu	0.4
Ni	0.04
Cr	0.15
Zn	0.35
Pb	0.15

was used. The balance of the analysis in this case comprises unburnt matter and waste scrap.

A waste slag of this type was charged into a shaft furnace along with 10 % $CaCl_2$ (3.6 % Ca + 6.4 % Cl) and heated at an oxygen shortage (countercurrent) by reduced operation. The offgas temperature of the shaft amounted to about 850°C. The calcined molten waste slag had the following analysis:

Component	Portion (%)
SiO_2	54
CaO	21
Al_2O_3	10
Fe_2O_3	4
MgO	2
Na_2O	3
SO_3	0.5
TiO_2	1.5
Cu	0.08
Ni	0.02
Cr	0.2
Zn	0.06
Pb	0.04

The calcined waste slag was mixed with 80 % steel slag in the liquid state, the latter having the following composition:

Component	Portion (%)
Steel	24
SiO_2	13
Al_2O_3	1
CaO	33
MgO	4
FeO	21
S	0.05
P	0.5
Cr	1

The mixed slag had the following composition:

Component	Portion (%)
Steel	20
SiO_2	21
CaO	31
Al_2O_3	3
FeO	18
MgO	3.5
Na_2O	0.6
SO_3	0.15
TiO_2	0.3
Cu	0.016
Ni	0.004
Cr	0.9

During the mixing procedure Zn and Pb evaporate practically quantitatively and could be recovered from the offgas.

That mixed slag was reduced in an OBM converter above a turbulent iron bath by means of carbon dissolved in the iron bath. The reduction heat as well as the waste heat losses in the gaseous phase were fed to the process very economically by partially burning the formed CO in the upper part of the converter.

The reduced slag had the following composition:

Component	Portion (%)
SiO_2	35
CaO	52
Al_2O_3	5
MgO	5
Na_2O	1
SO_3	0.25
TiO_2	0.5
Cr	0.03

The heavy metals Cu and Ni no longer were detectable in the reduced slag by means of X-ray fluorescence analysis (detection limit approx. 100 ppm).

The water-spray granulated slag proved to be a readily hydraulically active mixed cement component. Approximately 10 % bauxite (Al_2O_3) was added to the liquid slag melt with a view to providing a mixed cement having an elevated early strength.

The regulus (pig iron) obtained had the following composition:

Component	Portion (%)
Cu	0.05
Ni	0.01
Cr	2.6
C	3.8
Fe	balance

The method was conducted in a manner that the carbon portion of the iron bath always ranged between 3 and 4 % by weight. The pig iron thus obtained constitutes a high-quality charging substance for the steel industry. Alternatively, a carbon-free, highly enriched ferro-chromium alloy may, in turn, be obtained by fractional reduction.

Claims:

1. A method for separating copper and heavy metals from waste incineration residues and slags, characterized in that the waste incineration and/or pyrolysis residues and slags, together with chlorine and/or chloride-containing substances, such as smoke gas purification residues, $CaCl_2$ from soda production, common salt, chlorine-containing organic solvents or sludges derived from electroplating, are heated to above 650°C under reducing conditions, whereupon Cu chlorides and volatile heavy metal chlorides, such as, e.g., $PbCl_2$ or $ZnCl_2$, are drawn off in the gaseous phase.

2. A method according to claim 1, characterized in that flush gases, in particular hot combustion offgases, are used at temperatures of between 650° and 1400° C for discharging the volatile chlorides.

3. A method according to claim 1 or 2, characterized in that the gaseous phase containing the volatile heavy metal chlorides are conducted via a filter and the heavy-metal-chloride-containing filter dust is dissolved in water and/or cemented with Fe scrap, whereupon the heavy-metal chlorides are extracted and/or the heavy metals are separated by fractional electrolysis and/or are fractionally distilled.

4. A method according to claim 1, 2 or 3, characterized in that heating is effected in a shaft furnace by means of combustion offgases in countercurrent.

5. A method according to any one of claims 1 to 4, characterized in that the heated solid residues are mixed with liquid steel slag or lime marl in amounts of from 10 to 40 % by weight, preferably about 20 % by weight, so as to form a mixed slag, wherein evaporating heavy metals that have remained, such as Pb and Zn, are separated from the gaseous phase and chlorides possibly dissolved in the mixed slag, such

as, e.g., $CaCl_2$, are oxidized under Cl_2 stripping and the mixed slag is reduced above a turbulent Fe bath having a C content ranging between 3 and 4 % by weight.

6. A method according to any one of claims 1 to 5, characterized in that the turbulent Fe bath is subjected to a fractional reduction for separating a ferro-chromium alloy.

7. A method according to any one of claims 1 to 6, characterized in that heating of the residues to temperatures of approximately 850°C is effected in a shaft furnace or in a rotary tubular kiln.

8. A method according to any one of claims 1 to 7, characterized in that the CO formed in the reduction of the mixed slag by the carbon dissolved in the Fe bath is used for further burning and heating the mixed slag and/or the residues.

9. A method according to any one of claims 1 to 8, characterized in that bauxite, or Al_2O_3, is added to the liquid mixed slag.

10. A method according to any one of claims 1 to 9, characterized in that heating is effected under subatmospheric pressure.